

Liquid polymorphism and density anomaly in a three-dimensional associating lattice gas

Mauricio Girardi*

Universidade Federal de Pelotas - UNIPAMPA/Bagé,

Rua Carlos Barbosa SN, CEP 96400-970, Bagé, RS, Brasil.

Aline L. Balladares†

Instituto de Física, Universidade Federal do Rio Grande do Sul,

CP 15051, CEP 9105-970, Porto Alegre, RS,

Brasil and Departament de Fisica Fonamental, Universitat de Barcelona

Vera B. Henriques‡

Instituto de Física, Universidade de São Paulo,

Caixa Postal 66318, 05315970, São Paulo, SP, Brazil

Marcia C. Barbosa§

Instituto de Física, Universidade Federal do Rio Grande do Sul,

CP 15051, CEP 9105-970, Porto Alegre, RS, Brasil.

Abstract

We investigate the phase diagram of a three-dimensional associating gas (*ALG*) model. This model combines orientational ice-like interactions and “van der Waals” that might be repulsive, representing, in this case, a penalty for distortion of hydrogen bonds. These interactions can be interpreted as two competing distances making the connection between this model and continuous isotropic soft-core potentials. We present Monte Carlo studies of the *ALG* model showing the presence of two liquid phase, two critical points and A density anomaly.

PACS numbers:

*Electronic address: mgirardi@fge.if.usp.br

†Electronic address: linelb@if.ufrgs.br

‡Electronic address: vhenriques@if.usp.br

§Electronic address: marcia.barbosa@ufrgs.br

I. INTRODUCTION

Water is an anomalous substance in many respects. Most liquids contract upon cooling. This is not the case of water, a liquid where the specific volume at ambient pressure starts to increase when cooled below $T = 4^{\circ}C$ [1]. Besides, in a certain range of pressures, water also exhibits an anomalous increase of compressibility and specific heat upon cooling [2]-[4]. Far less known are its dynamics anomalies: while for most materials diffusivity decreases with increasing pressure, liquid water has an opposite behavior in a large region of the phase diagram [5]-[13].

It was proposed a few years ago that these anomalies are related to a second critical point between two liquid phases, a low density liquid (LDL) and a high density liquid (HDL) [14]. This critical point was discovered by computer simulations. This work suggests that the critical point is located at the supercooled region beyond the line of homogeneous nucleation and thus cannot be experimentally measured. Inspite of this limitation, this hypothesis has been supported by indirect experimental results [15][16].

Water, however, is not an isolated case. There are other examples of tetrahedrally bonded molecular liquids, such as phosphorus [17, 18] and amorphous silica [19], that also are good candidates for having two liquid phases. Moreover, other materials such as liquid metals [20] and graphite [21] also exhibit thermodynamic anomalies. Unfortunately a coherent and general interpretation of the low density liquid and high density liquid phases is still missing.

What kind of potential would be appropriated for describing the tetrahedrally bonded molecular liquids, capturing the presence of thermodynamic anomalies? Realistic simulations of water [22]-[24] have achieved a good accuracy in describing the thermodynamic and dynamic anomalies of water. However, due to the high number of microscopic details taken into account in these models, it becomes difficult to discriminate what is essential to explain the anomalies. On the other extreme, a number of isotropic models were proposed as the simplest framework to understand the physics of the liquid-liquid phase transition and liquid state anomalies. From the desire of constructing a simple two-body isotropic potential capable of describing the complicated behavior present in water-like molecules, a number of models in which single component systems of particles interact via core-softened (CS) potentials have been proposed. They possess a repulsive core that exhibits a region of softening where the slope changes dramatically. This region can be a shoulder or a ramp

[25]-[43]. Unfortunately, these models, even when successful in showing density anomaly and two liquid phases, fail in providing the connection between the isotropic effective potential and the realistic potential of water.

It would, therefore, be desirable to have a theoretical framework which retains the simplicity of the core-softened potentials but accommodates the tetrahedral structure and the role played by the hydrogen bonds present in water. A number of lattice models in which the tetrahedral structure and the hydrogen bonds are present have been studied [44]-[48]. One of them, is the three-dimensional model proposed by Roberts and Debenedetti [46] and further studied by Petti and Buzano [47] defined on the body centered cubic lattice. According to their approach, the energy between two bonded molecules rises when a third particle is introduced on A site neighbour to the bond. Using a cluster mean-field approximation, they were able to find the density anomaly and two liquid phases.

In order to investigate the mixtures of water with other chemical species as that present in a number of biological and industrial processes, it would be interesting to have a simpler model capable of capturing the same essential features observed in water and also being able to bridge the gap between the realistic models for water and the isotropic softened-core potentials.

Thus, in this paper we investigate a three-dimensional associating lattice-gas model that can fulfill both requirements. Our model system is a lattice gas with ice variables [49] which allows for a low density ordered structure. Competition between the filling up of the lattice and the formation of an open four-bonded orientational structure is naturally introduced in terms of the ice bonding variables, and no *ad hoc* introduction of density or bond strength variations is needed. In that sense, our approach bares some resemblance to that of continuous softened-core models [50, 51, 52]. Using this simple model we are able to find two liquid phases, two critical points and the density anomaly. The remainder of the paper goes as follows. In sec. II the model is introduced and the simulation details are given. Sec. III is devoted to the main results and conclusion ends this session.

II. THE MODEL

We consider a body-centered cubic lattice with V sites, where each site can be either empty or filled by a water molecule. Associated to each site there are two kinds of variables:

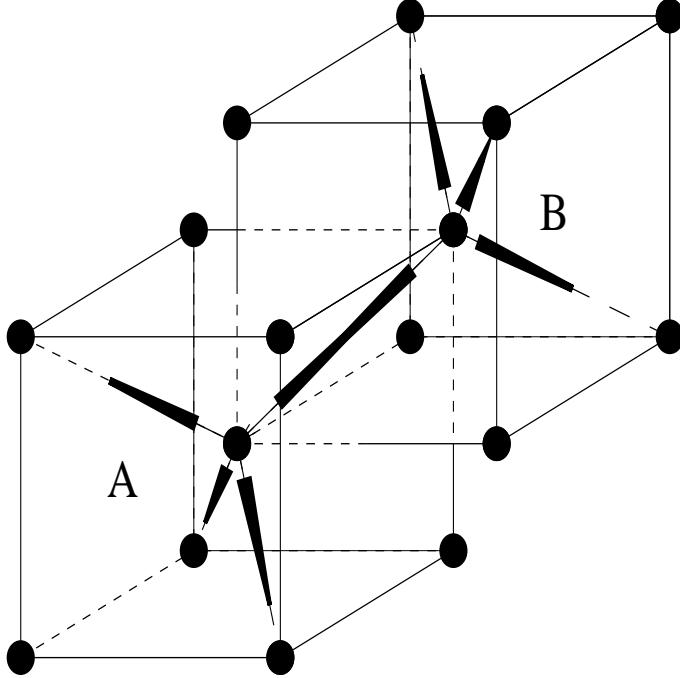


FIG. 1: The two possible states of the water molecules in the body centered cubic lattice. *A* and *B* molecules are forming an hydrogen bond since two of their arms are pointing each other.

an occupational variables, σ_i , and an orientational one, τ_i^{ij} . For $n_i = 0$ the i site is empty, and $n_i = 1$ represents an occupied site. The orientational state of particle i is defined by the configuration of its bonding and non-bonding arms, as illustrated in Fig 1. Four of them are the usual ice bonding arms with $\tau_i^{ij} = 1$ distributed in a tetrahedral arrangement, and four additional arms are taken as inert or non-bonding ($\tau_i^{ij}=0$). Therefore, each molecule can be in one of two possible states *A* and *B* are shown illustrated in Fig. 1. A potential energy ε is associated to any pair of occupied nearest-neighbor (NN) sites, mimicking the van der Waals potential. Here, water molecules have four indistinguishable arms that can form hydrogen-bonds (HB). An HB is formed when two arms of NN molecules are pointing to each other with $\tau_i^{ij} = 1$. An energy γ is assigned to each formed HB.

In resume the total energy of the system is given by:

$$E = \sum_{(i,j)} n_i n_j (\varepsilon + \gamma \tau_i^{ij} \tau_j^{ji}) . \quad (1)$$

The interaction parameters were chosen to be $\varepsilon > 0$ and $\gamma < 0$, which implies in an energetic penalty on neighbors that do not form *HBS*. From this condition results the presence of

two liquid phases and the density anomaly.

The ground state of the system can be inferred by simply inspecting the equation 1, and taking account an external chemical potential μ . At zero temperature, the grand potential per volume is $\Omega = e + \mu\rho$, where ρ is the water density and $e = E/V$. At very low values of the chemical potential, the lattice is empty and the system is in the gas phase. As the chemical potential increases, at $\mu = -2(\varepsilon + \gamma)$, a gas phase with $\rho = 0$ and a low density liquid (*LDL*) with $\rho = 1/2$ coexist. In this case, each molecule in the *LDL* phase has four occupied *NN* sites, forming four *HBs*, and the energy per site is $e = \varepsilon + \gamma$. As the chemical potential increases even further a competition between the chemical potential that favors filling up the lattice and the HB penalty that favors molecules with only four *NN* sites appears. At $\mu = -6\varepsilon - 2\gamma$, the *LDL* phase coexists with a high density liquid (*HDL*) with $\rho = 1$. In the *HDL*, each molecule has eight *NN* occupied sites, but forms only four *HBs*. The other four non-bonded molecules are repealed, which can be viewed as an effective weakening of the hydrogen bonds due to distortions of the electronic orbitals of the bonded molecules. The energy per molecule is then $e = 4\varepsilon + 2\gamma$.

Our model may be interpreted in terms of some sort of average soft-core potential for large hydrogen-bond energies. The low density phase implies an average interparticle distance $\overline{d_{LD}} = \rho_{LD}^{-1/3} = 2^{1/3}$, whereas for the high density phase we have $\overline{d_{HD}} = \rho_{HD}^{-1/3} = 1$. The corresponding energies per pair of particles are $e_p^{LDL} = \varepsilon + \gamma$ and $e_p^{HDL} = \varepsilon + \gamma/2$ respectively. Figure 2 illustrates this effective pair potential for the case of $\gamma/\varepsilon = -2$. The hard core is offered by the lattice, since two particles cannot occupy the same site.

The system pressure P can be calculated from the grand potential since $\Omega = -P$. At the gas-*LDL* coexistence, $P = 0$ and at *LDL-HDL* coexistence point, $P = 2\varepsilon$.

The model properties for finite temperatures were obtained through Monte Carlo simulations in the grand-canonical ensemble (chemical potential and temperature were kept constant). The total number of molecules is allowed to change in time by means of the Metropolis algorithm, where in one time unit (1 Monte Carlo step) we test all lattice sites in order to insert or exclude one water molecule. The insertion and exclusion transition rates are written as $w(\text{insertion}) = \exp(-\Delta\phi)$ and $w(\text{exclusion}) = 1$ if $\Delta\phi > 0$, and $w(\text{insertion}) = 1$ and $w(\text{exclusion}) = \exp(+\Delta\phi)$ if $\Delta\phi < 0$. Here $\Delta\phi = \beta(e_{\text{molecule}} - \mu) - \ln(2)$, where e_{molecule} is the energy of the included (or excluded) molecule, and the factor $\ln(2)$ guarantees the detailed balance.

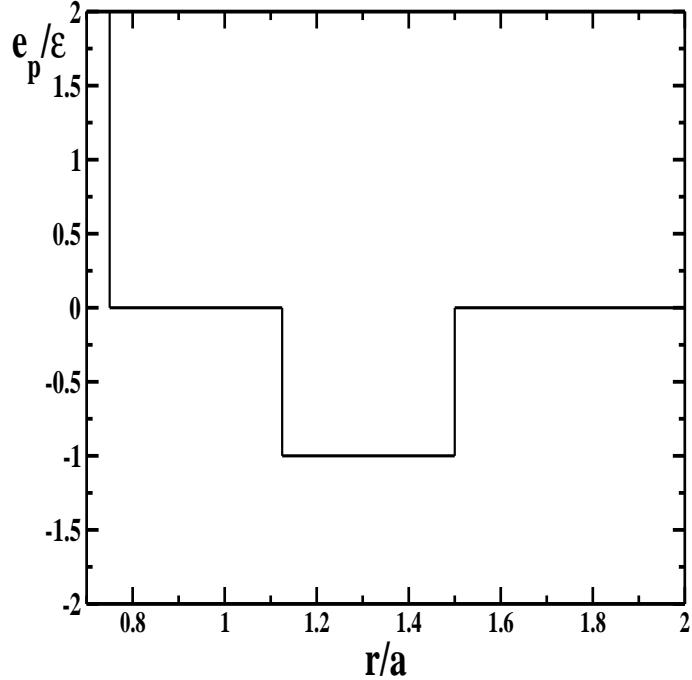


FIG. 2: Effective potential vs inter-particle distance for $\gamma/\varepsilon = -2$. The corresponding energies per pair of particles are $e_p^{LDL} = \varepsilon + \gamma$ and $e_p^{HDL} = \varepsilon + \gamma/2$ for *LDL* and *HDL* respectively.

The simulations were carried out for lattices with linear size $L = 10$, and the interaction parameters were set to $\gamma/\varepsilon = -2$. Runs were of the order of 10^4 Monte Carlo steps. Some test runs were done for $L=20$, showing no relevant change in the critical temperatures. A detailed study of the model properties and the full phase diagrams was undertaken for an $L=10$ lattice.

In order to obtain the pressure-temperature phase diagram of the model, the pressure was calculated from the simulation data. By numerical integration of the Gibbs-Duhem relation, $SdT - VdP + Nd\mu = 0$ at fixed temperature, we obtain $P(\rho, T)$, using the condition that $P = 0$ at $\rho = 0$. Since the model presents two first-order phase transitions (from gas to *LDL*, and from *LDL* to *HDL* phases), the curves ρ versus μ have two discontinuities and hysteresis loops. The hystereses were observed when the simulations were started at different initial conditions for a given chemical potential around the transition point.

III. RESULTS AND CONCLUSIONS

The model properties for finite temperatures that were obtained through simulations at constant temperature and chemical potential go as follows. For sufficiently low values of the chemical potential and at low temperatures, all attempts to insert molecules are frustrated, and the total density ρ remains equal to zero. By increasing the value of μ , the molecules begin to enter in the system, increasing ρ and leading to two first-order transitions, one between the gas and the *LDL* phases and another between the *LDL* and *HDL* phases. The dependence between ρ and the reduced chemical potential $\bar{\mu} = \mu/\varepsilon$ for some temperatures is illustrated in Fig. 3a. Similarly the number of hydrogen bonds per site is illustrated in Fig. 3b. The transition between one hydrogen bond per site to two hydrogen bonds per site occurs at the *LDL-HDL* phase transition. The coexistence of the gas and *LDL* phases and the *LDL* and the *HDL* phases were then obtained from this data.

In order to confirm the loci of the coexistence lines and the critical points, the histograms of the densities were collected during a simulation run. The histograms for four different temperatures and chemical potentials are shown in Fig. 4 for illustration. Near a first-order phase transition, mainly inside the metastable region, the histogram is double-peaked, and the system density fluctuates around two characteristic values. One can obtain the coexistence lines by finding the chemical potential in which both peaks have the same height (Figs. 4a and 4c). As the temperature approaches the critical value, the peaks converge to a single one, and a homogeneous phase appears (Figs. 4b and 4d).

In Fig. 5 we exhibit the reduced pressure, $\bar{P} = P/\varepsilon$, versus density isotherms. The gas-*LDL* and *LDL-HDL* first-order phase transitions are evidenced by the presence of plateaus in the $\bar{P} \text{ vs. } \rho$ curves at low reduced temperatures, $\bar{T} = T/k_B$.

The plot of density versus reduced temperature at constant pressures shows that an inversion of the behavior of density as a function of temperature takes place at intermediate pressures, in the *LDL* phase. At smaller pressures, density decreases with temperature, whereas at higher pressures, density increases with temperature. This yields a temperature of maximum density for a fixed pressure, *TMD*, in the higher range of pressures, which we illustrate in Fig. 6.

The pressure-temperature phase diagram is illustrated in Fig. 7. The gas, *LDL* and *HDL* phases are shown together with the two coexistence lines, the two critical points and the

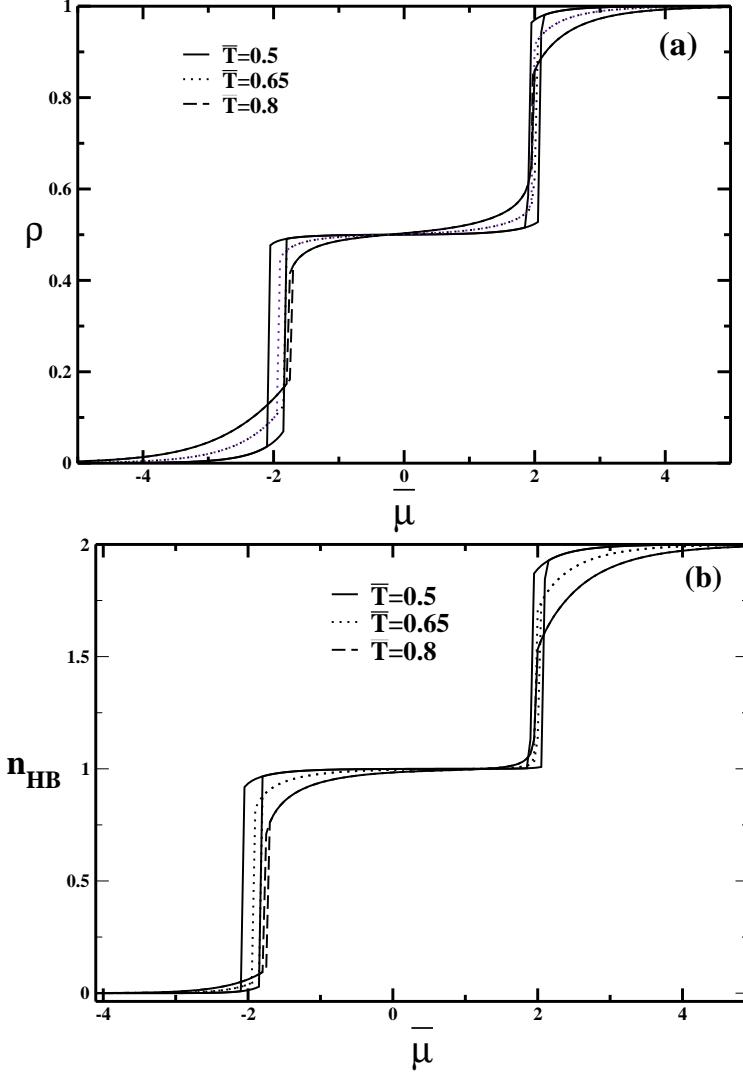


FIG. 3: (a) Density isotherms vs. reduced chemical potential for different temperatures. (b) Number of bonds per site vs. reduced chemical potential for different temperatures. ρ is given in units of lattice space and the temperature is in units of k_B .

line of temperature of maximum density (TMD) as a function of pressure. Density versus reduced temperature illustrating the two coexistence regions and the two critical points are shown in Fig. 8.

We have shown that it is possible to incorporate some of the microscopic properties of true water molecules into a very simple minimal model that still contains some of the ingredients of real water without having its whole complexity.

The model includes orientational and occupational variables, and guarantees the local distribution of hydrogens on molecular bonds, without the need of increasing the volume

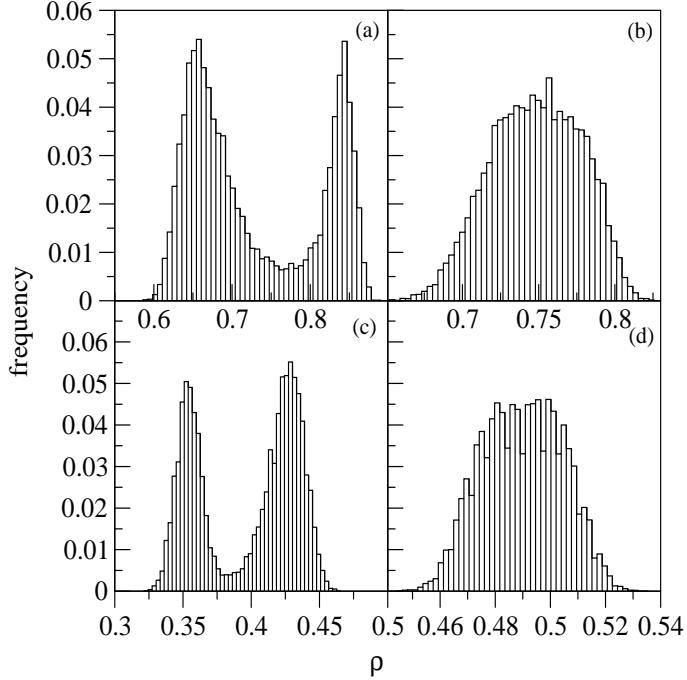


FIG. 4: Histograms of the total density ρ . (a) the coexistence between *LDL* and *HDL* phases at $T = 0.8$ and (b) an homogeneous phase at $T = 1.0$ near the *LDL* – *HDL* critical temperature. (c) the coexistence between *gas* and *LDL* phases at $T = 1.2$ and (d) an homogeneous phase at $T = 1.4$, near the *gas* – *LDL* critical temperature.

artificially or introducing artificial orientational variables [45]. In spite of the absence of an orientational order-disorder transition [53], the model presents liquid-liquid coexistence, with slightly positive slope in the pressure-temperature plane, accompanied by a line of maximum density on the low density side, a feature expected for real water. Besides, this study points out to the fact that the presence of a density anomaly, with the thermal expansion coefficient $\alpha < 0$, on the low temperature side, and as a consequence, $(\frac{\partial S}{\partial p})_T > 0$, *does not* imply a negative slope of the liquid-liquid line, contrasting with the results for most studies of metastable liquid-liquid coexistence in models for water, which suggest a transition line with negative gradient [26].

The presence of both a density anomaly and two liquid phases in our model begs the question of which features of this potential are responsible for such behaviour. Averaged over orientational degrees of freedom, our model can be seen as some kind of shoulder potential, with the liquid-liquid coexistence line being present only for a repulsive “van der

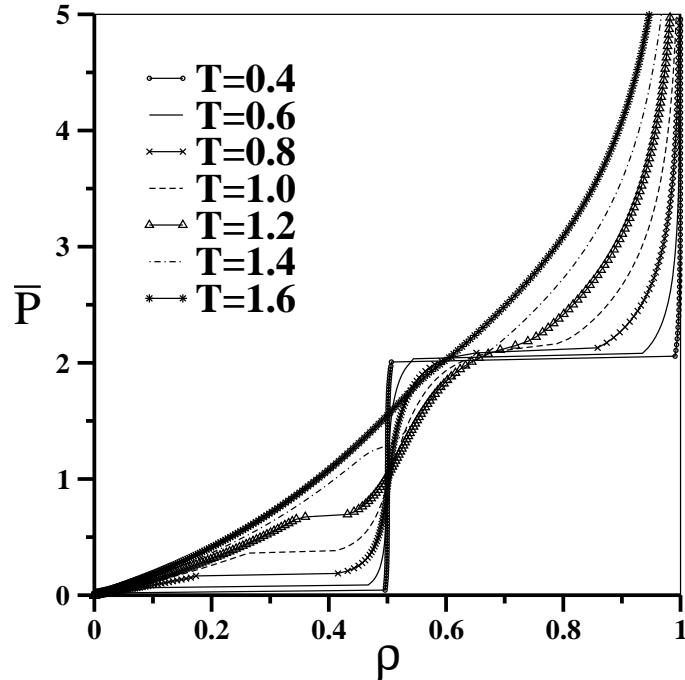


FIG. 5: Reduced pressure as a function of the total density ρ for some values of \bar{T} .

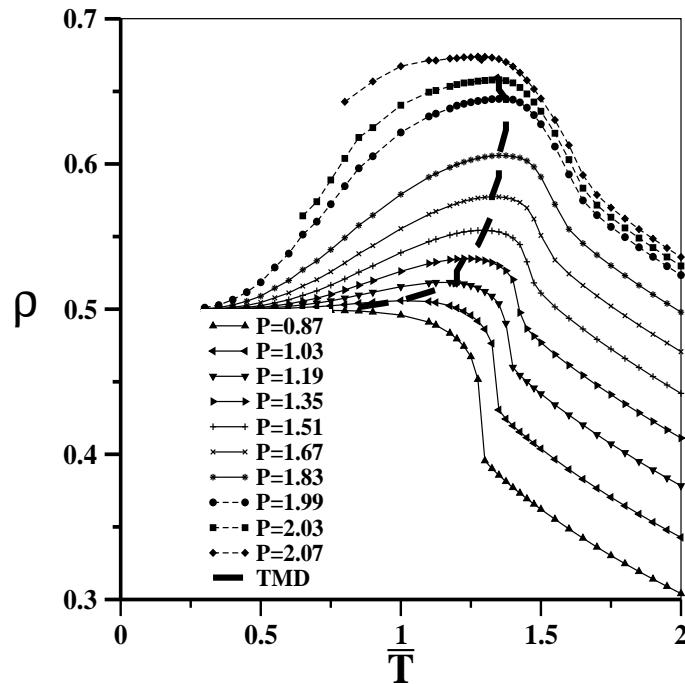


FIG. 6: Total density as a function of reduced temperature at constant values of the reduced pressure. The maximum in the curves give the temperature of maximum density for a given pressure.

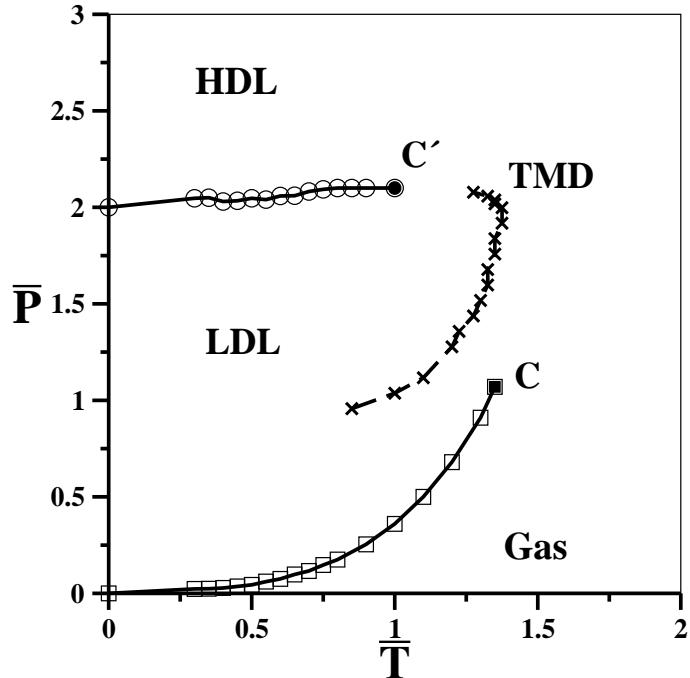


FIG. 7: Reduced pressure versus reduced temperature phase diagram. The gas-*LDL* and *LDL*-*HDL* coexistence lines, the two critical points and the TMD line are shown.

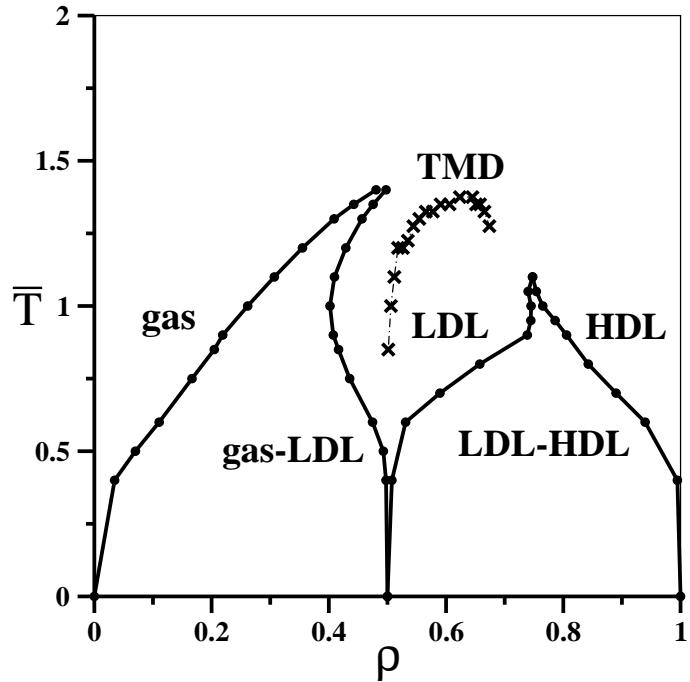


FIG. 8: Density as versus reduced temperature illustrating the two coexistence regions, the two critical points and the TMD line.

Waals" potential. The same was indeed observed for continuous step pair potentials [27][30], for which, however, the density anomaly is absent. On the other hand, a density anomaly has been observed in a number of shoulder-like lattice models in which the major ingredient is the competition between two scales [31, 32, 33]. This feature is present in our case. Therefore it seems that the competition between two scales is the major ingredient that warrantIES the presence of the density anomaly. If, in addition, the model has an attractive interaction, two liquid phases and two critical points emerge.

Acknowledgments

This work was supported by the Brazilian science agencies CNPq, FINEP, Fapesp and Fapergs.

- [1] R. Waller, *Essays of Natural Experiments*, Johnson Reprint corporation, New York (1964).
- [2] F. X. Prielmeier, E. W. Lang, R. J. Speedy and H. -D. Lüdemann, Phys. Rev. Lett. **59**, 1128 (1987).
- [3] F. X. Prielmeier, E. W. Lang, R. J. Speedy, H. -D. Lüdemann and B. Bunsenges, Phys. Chem. **92**, 1111 (1988).
- [4] L. Haar, J. S. Gallagher, G. S. Kell, NBS/NRC Steam Tables. Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units, Hemisphere Publishing Co., Washington DC, 1984, pp271-276.
- [5] F. W. Starr, F. Sciortino and H. E. Stanley, Phys. Rev. E **60**, 6757 (1999); F. W. Starr, S. T. Harrington, F. Sciortino and H. E. Stanley, Phys. Rev. Lett. **82**, 3629 (1999).
- [6] P. Gallo, F. Sciortino, P. Tartaglia and S. -H. Chen, Phys. Rev. Lett. **76**, 2730 (1996); F. Sciortino, P. Gallo, P. Tartaglia and S. -H. Chen, Phys. Rev. E **54**, 6331 (1996); S. -H. Chen, F. Sciortino and P. Tartaglia, *ibid.* **56**, 4231 (1997); F. Sciortino, L. Fabbian, S. -H. Chen and P. Tartaglia *ibid.* **56**, 5397 (1997).
- [7] S. Harrington, P. H. Poole, F. Sciortino and H. E. Stanley, J. Chem. Phys. **107**, 7443 (1997).
- [8] F. Sciortino, A. Geiger and H. E. Stanley, Nature (London) **354**, 218 (1991); J. Chem Phys.

96, 3857 (1992).

[9] J. R. Errington and P. G. Debenedetti, *Nature (London)* **409**, 318 (2001).

[10] P. A. Netz, F. W. Starr, H. E. Stanley and M. C. Barbosa, *J. Chem. Phys.* **115**, 344 (2001).

[11] P. A. Netz, F. W. Starr, M. C. Barbosa and H. E. Stanley, *Physica A* **314**, 470 (2002).

[12] H. E. Stanley, M. C. Barbosa, S. Mossa, P. A. Netz, F. Sciortino, F. W. Starr and M. Yamada, *Physica A* **315**, 281 (2002).

[13] P. A. Netz, F. W. Starr, M. C. Barbosa and H. E. Stanley, *J. Mol. Liquids* **101**, 159 (2002).

[14] P. H. Poole, F. Sciortino, U. Essmann and H. E. Stanley, *Nature* **360**, 324 (1992); *Phys. Rev. E* **48**, 3799 (1993); F. Sciortino, P. H. Poole, U. Essmann and H. E. Stanley, *ibid.* **55**, 727 (1997); S. Harrington, R. Zhang, P. H. Poole, F. Sciortino and H. E. Stanley, *Phys. Rev. Lett.* **78**, 2409 (1997).

[15] O. Mishima and H. E. Stanley, *Nature* **396**, 329 (1998).

[16] R. J. Speedy and C. A. Angell, *J. Chem. Phys.* **65**, 851 (1976).

[17] Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamakata and K. Funakoshi, *Nature* **403**, 170 (2000).

[18] G. Monaco, S. Falconi, W. A. Crichton and M. Mezouar, *Phys. Rev. Lett.* **90**, 255701 (2003).

[19] D. J. Lacks, *Phys. Rev. Lett.* **84**, 4629 (2000).

[20] P. T. Cummings and G. Stell, *Mol. Phys.* **43**, 1267 (1981).

[21] M. Togaya, *Phys. Rev. Lett.* **79**, 2474 (1997).

[22] F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **60**, 1545 (1974).

[23] H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).

[24] M. W. Mahoney and W. L. Jorgensen, *J. Chem. Phys.* **112**, 8910 (2000).

[25] M. R. Sadr-Lahijany, A. Scala, S. V. Buldyrev and H. E. Stanley, *Phys. Rev. Lett.* **81**, 4895 (1998); M. R. Sadr-Lahijany, A. Scala, S. V. Buldyrev and H. E. Stanley, *Phys. Rev. E* **60**, 6714 (1999).

[26] A. Scala, M. R. Sadr-Lahijany, N. Giovambattista, S. V. Buldyrev and H. E. Stanley, *J. Stat. Phys.* **100**, 97 (2000); A. Scala, M. R. Sadr-Lahijany, N. Giovambattista, S. V. Buldyrev and H. E. Stanley, *Phys. Rev. E* **63**, 041202 (2001).

[27] G. Franzese, G. Malescio, A. Skibinsky, S. V. Buldyrev and H. E. Stanley, *Nature* **409**, 692 (2001).

[28] S. V. Buldyrev, G. Franzese, N. Giovambattista, G. Malescio, M. R. Sadr-Lahijany, A. Scala,

A. Skibinsky and H. E. Stanley, *Physica A* **304**, 23 (2002).

[29] S. V. Buldyrev and H. E. Stanley, *Physica A* **330**, 124 (2003).

[30] G. Franzese, G. Malescio, A. Skibinsky, S. V. Buldyrev and H. E. Stanley, *Phys. Rev. E* **66**, 051206 (2002).

[31] A. Balladares and M. C. Barbosa, *J. Phys.: Cond. Matt.* **16**, 8811 (2004).

[32] A. B. de Oliveira and M. C. Barbosa, *J. Phys.: Cond. Matt.* **17**, 399 (2005).

[33] A. B. de Oliveira, P. A. Netz, T. Colla, and M. C. Barbosa, *J. Chem. Phys.* **124**, 084505 (2006).

[34] V. B. Henriques and M. C. Barbosa, *Phys. Rev. E* **71**, 031504 (2005)

[35] V. B. Henriques, N. Guissoni, M. A. Barbosa, M. Thielo and M. C. Barbosa, *Mol. Phys.* **103**, 3001 (2005).

[36] A. Skibinsky, S. V. Buldyrev, G. Franzese, G. Malescio and H. E. Stanley, *Phys. Rev. E* **69**, 061206 (2004).

[37] G. Malescio, G. Franzese, A. Skibinsky, S. V. Buldyrev and H. E. Stanley, *Phys. Rev. E* **71**, 061504 (2005).

[38] P. C. Hemmer and G. Stell, *Phys. Rev. Lett.* **24**, 1284 (1970); G. Stell and P. C. Hemmer, *J. Chem. Phys.* **56**, 4274 (1972); J. M. Kincaid, G. Stell and C. K. Hall, *ibid.* **65**, 2161 (1976); J. M. Kincaid, G. Stell and E. Goldmark, *ibid.* **65**, 2172 (1976); C. K. Hall and G. Stell, *Phys. Rev. A* **7**, 1679 (1973).

[39] E. A. Jagla, *Phys. Rev. E* **58**, 1478 (1998); E. A. Jagla, *J. Chem. Phys.* **110**, 451 (1999); E. A. Jagla, *J. Chem. Phys.* **111**, 8980 (1999); E. A. Jagla, *Phys. Rev. E* **63**, 061501 (2001); E. A. Jagla, *Phys. Rev. E* **63**, 061509 (2001).

[40] N. B. Wilding and J. E. Magee, *Phys. Rev. E* **66**, 031509 (2002).

[41] P. Kumar, S. V. Buldyrev, F. Sciortino, E. Zaccarelli and H. E. Stanley, *Phys. Rev. E* **72**, 021501 (2005).

[42] P. J. Camp, *Phys. Rev. E* **68**, 061506 (2003).

[43] P. J. Camp, *Phys. Rev. E* **71**, 031507 (2005).

[44] G. M. Bell, *J. Phys. C: Solid State Phys.* **5**, 889 (1972).

[45] N. A. M. Besselink and J. Lyklema, *J. Phys. Chem.* **98**, 11610 (1994). The authors investigate a related model in three dimensions but their interest lie in different properties than those under study in this paper.

- [46] C. J. Roberts and P. G. Debenedetti, *J. Chem. Phys.* **105**, 658 (1996).
- [47] M. Pretti and C. Buzano, *J. Chem. Phys.* **121**, 11856 (2004).
- [48] M. Pretti and C. Buzano, *J. Chem. Phys.* **123**, 24506 (2005).
- [49] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).
- [50] K. A. T. Silverstein, A. D. J. Haymet and K. A. Dill, *J. Am. Chem. Soc.* **120**, 3166 (1998).
- [51] T. M. Truskett, P. G. Debenedetti, S. Sastry and S. Torquato, *J. Chem. Phys.* **111**, 2647 (1999).
- [52] T. M. Truskett and K. A. Dill, *J. Chem. Phys.* **117**, 5101 (2002).
- [53] W. Nadler and T. Krausche *Phys. Rev. A* **44**, R7888 (1991); N. Guisoni and V. B. Henriques, *Braz. J. Phys.* **30**, 736 (2000).